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2005 J. Phys.: Conf. Ser. 15 45

(http://iopscience.iop.org/1742-6596/15/1/008)

Institute of Physics Publishing Journal of Physics: Conference Series **15** (2005) 45–50
doi:10.1088/1742-6596/15/1/008 Sensors & their Applications XIII

Successive ionic layer deposition: possibilities for gas sensor applications

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Abstract. In this paper we discuss results of research related to design of successive ionic layer deposition (SILD) technology for both preparing porous nano-structured SnO_2 films, and surface modification of SnO_2 films deposited by spray pyrolysis. This new method of metal oxide deposition has exited high interest, because of this method simplicity, cheapness, and ability to deposit thin nano-structured films on rough surfaces. Method of successive ionic layer deposition (SILD) consists essentially of repeated successive treatments of the conductive or dielectric substrates by solutions of various salts, which form on the substrate surface poorly soluble compounds. It was shown that SILD technology is effective method for above mentioned purposes.

1. Introduction

The progress in catalysis and gas sensing thus can not proceed without the deep knowledge of the nanoscale architecture of active sites at the catalyst or gas sensing surfaces. In order to optimize performances of these materials it is needed to develop a strategy to master their surface, in particular, form and stabilize active sites in their more active and selective configuration, that may allow a full control of the catalytic and gas detection process. A rational and systematic approach to form and stabilize active sites in their most active and selective configuration may allow better control catalytic and gas sensing processes. The synthesis of sequentially added nanolayers of noble metals and special inorganic compounds with a prescribed composition and thickness on the surface of standard catalytic and gas sensing materials (metal oxides) is one of the paramount problems in the preparative chemistry of solids for these purposes [1,2]. This is due to the fact that such nanolayers significantly alter a number of important properties of the surface and, therefore, are utilized in preparing sorbents, catalysts, and gas sensing materials. For example such optimization is necessary for improvement of sensitivity, selectivity and temporal stability of electrical response of gas sensors. For these purposes various additives may be used. Depending on the required result, such elements as noble metals (Ag, Au, Pd, Pt), transition metals (Fe, Mn, Co, Ni, Mo, Cu), oxides of W, Ti, P, and so can be applied [1,2]. These additives can act as a promoters, catalysts, surface sites for adsorption of oxygen and detected gas with following spillover of adsorbed species, or as elements promoting the improvement of porosity of the gas sensing matrix, thermal stability of powders and film microstructure, and so on.

For preparing nanolayers and incorporating a second component into metal oxide, various

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methods can be used. Many methods have already been tested for this purpose, for example bulk doping during calcination, sol-gel technology, spray pyrolysis deposition, thermal evaporation, CVD, laser ablation, magnetron sputtering, electroless addition. With the help of these methods, it was possible to form on a surface of metal oxides surface clusters of various components with sizes from 0.1 to 8 nm [1]. However, in many cases these traditional approaches were not effective. Thin film deposition methods such as chemical vapor deposition (CVD), MOCVD, molecular beam epitaxy (MBE), magnetron sputtering, or vacuum evaporation, are very cumbersome and inefficient for deposition of complex materials. The difficulty to deposit various elements uniformly on the surface of dispersed particles, especially of such materials as nanoscaled powders and highly porous materials, is another great limitation of most of the standard deposition methods. Using other standard methods, for example electroless addition we have trouble with completely controllable deposition of the layers with small thickness, especially in the range of nm sizes. The complexity and high cost of these traditional film deposition techniques severely limits the ability to systematically experiment with modification of film composition over wide ranges and to quickly identify film compositions with optimum gas sensing and catalytic characteristics. This limits the ability to systematically study the nature of gas sensitive and catalytic effects as well. Consequently, the selection of suitable base materials, metal catalysts, promoters and additives relies on a time consuming and costly empirical approach. When we use the methods of bulk doping (sol-gel method) the changes of both structural and electrophysical properties take place simultaneously with surface modification. As a result, the problem of understanding of the role of surface modification in catalytic and gas sensing phenomena appear during model experiments. Besides, sol-gel deposition involves a multi-stage process demanding long duration. *Therefore, the development of new or improved materials for catalysis and gas sensor applications requires a search for novel and innovative approaches to the nano-scale design of these materials. The use of the technology of surface modification by successive ionic layer deposition (SILD) method is such an innovative approach*

2. Peculiarities of SILD technology

The distinguishing characteristic of SILD method is the use of alternating aqueous solutions (a metal salt solution, followed by a hydrolyzing or sulfidizing solution). The SILD method consists essentially of repeated successive treatments of the substrate surface with solution of various salts such as acetates, chlorides, and nitrates of various metals [3]. A significant limitation in SILD deposition of oxide thin films seems to be that upon repeated treatment of the growing film, which is necessary for the synthesis of the next layer, the film is redissolved (at least partially) in the solution of the metal salt. For resolving this problem Tolstoy [4,5] suggested the use of a metal salt in a lower oxidation state. For this purpose it was proposed to oxidize the metal ions during film formation, or for cations such as Cu^{2+}, Zn^{2+}, La^{3+} to synthesize the poorly soluble layer of hydroxides - peroxides. It was proposed the six routs of the synthesis of hard to dissolve hydrated metal–oxygen compounds. They are followings:

1) reactions of adsorbed metal cations with H_2O_2 (OH^-), which was used to synthesize CuO_{1+x}, ZnO_{1+x}, and $La(OH)_x(OOH)_y$;

2) oxidation of the adsorbed metal layer by a H_2O_2 solution, resulting in the subsequent formation of a layer of the metal peroxide (by example of the $Ce(OH)_x(OOH)_{4-x}$ layers), metal oxides ($SnO_2 \cdot nH_2O$, $Tl_2O_3 \cdot nH_2O$, $PbO_2 \cdot nH_2O$) or metal hydroxides (FeOOH);

3) reactions of adsorbed metal cation (La_{aq}^{3+}) with peroxianion (NbO_8^{3-}) with formation of hard-to dissolve compound $La_xNbO_y \cdot nH_2O$;

4) oxidation of adsorbed metal cation (Ce_{aq}^{3+}) by peroxianion (NbO_8^{3-})with the following interaction and formation of $Ce_xNbO_y \cdot nH_2O$;

5) reduction of adsorbed anions by cations (e.g., reduction of MnO_4 by Mn^{2+} leads to formation of a $MnO_2 \cdot nH_2O$ layer and reduction of MoO_4^{2-} by a $SnCl_2$ solution results in formation of $Sn_xMoO_y \cdot nH_2O$);

6) reduction of adsorbed anions of heteropoly oxometalates (the $H_7PW_{12}O_{42}$ reduced by a $SnCl_2$ solution transforms into hybride isopoly (Sn-O)-heteropoly (H-P-W-O-) compound.

So, this method is based on the acts of adsorption of cations and then anions from solutions, whose interaction on the substrate surface produces poorly soluble compounds, such as hydroxides, peroxides and oxides hydrates. Then, the samples are being washed with distilled water, which remove excess of salt, treated with a H_2O_2 (OH-) solution, and again washed. One such treatment comprises one deposition cycle. The duration of each treatment depends on the time of every stage of sorption and removal of excess reagents. For different materials, this time can be varied from 1 to 10 min. Ellipsometric measurements have shown that after each cycle a layer of peroxicomplexes or hydroxides of metals with thickness 0.4-1.5 nm can be deposited on the surface of substrate. So, the simple notion of SILD chemistry is based on processes of hydroxylation of growing layer, proton-metal cation exchange between hydroxylated layer and water solution, and additional oxidizing by hydrogen peroxide resulted in higher oxidation state of chemisorbed metal ion and forming poor-soluble peroxicomplexes.

The indicated thickness of peroxicomplexes or hydroxides depends on the type of deposited metal. The film thickness' dependence on the number of deposition cycles follows a linear law [4]. Thus, this method allows to control the film thickness with high precision via the number of ionic deposition cycles. On relatively weak heating (100-400^{o}C), these compounds release water and transform into corresponding oxides. Some compounds, which can be interesting for gas sensor applications, obtained by SILD method, are shown in the Table 1.

Table 1. Metals and compounds deposited by SILD

Material	Precursors	Temperature for transformation in metal oxide, ^{o}C	Thickness of one layer, nm	Reference
SnO_2	SnF_2	300-350	0.5-1.5	[7]
CuO_2	$Cu(NH_3)_2$; $Cu(NO_3)_2$; $Cu(acc)_2$	150-200	0.3-1.5	[9]
CoO	$CoSO_4$			[9]
SnWPO	$SnCl_2 + H_3PW_{12}O_{40}$	400-500		[8]
La_XNbO_Y	$La(acc)_3 + Nb(OH)_5H_2O_2$	350-400	~0.6	[4]
MnO_2	$MnCl_2$; $KMnO_4$		~1.0	[9,12]
CeO_2	$Ce(NO_3)_3$; $Ce(acc)_3$	300-350	0.3-1.5	[10]
Fe_2O_3	$(NH_4)_2[Fe(SO_4)_2]$	250-300	0.3-0.5	[11]
Ag	$AgNO_3$			
Pd	$PdCl_2$			

3. Advantages of SILD technology

The main advantage of such chemical route is conditioned by the fact that reaction of cation metal adsorption during second step of deposition cycle is automatically stopped when monolayer coverage is attained. So here the some type of self-assembly is observed. In principle, this is intended to allow ion-by-ion growth of the compound film via sequential addition of individual atomic layers.

This synthesis can be carried out under “mild” conditions, at room temperature, in a simple apparatus, using for deposition simple, inexpensive precursors and solutions with pH near to neutral. The SILD method is a clean and innovative process with low emissions, ready availability, and low maintenance costs. Dilute solutions including cation- and anion-reagents and stripping water after SILD synthesis can be utilized easily by simple mixing and filtration. This method does not require electrical current. Therefore, the particles used for surface modification can be in the solution in suspension state. As a result, this procedure allows to deposit nanolayers or nanoclusters of noble metals and metal oxides on the developed surface, for instance, on the surface of porous materials and disperse grains (powders).

The SILD method does not possess high deposition rate in comparison with other chemical methods of deposition such as electrochemical deposition, chemical deposition, and so on [3]. However, this property is not required for surface modification, especially by nanoclusters and nanolayers. Precise monitoring of both the size and composition of deposited clusters is more important for surface modification. It gives this method great advantages in comparison with many other methods used for surface modification of metal oxides. Therefore, the SILD-based technique will have the potential for new nanoscale products and innovative materials with nano-modified surface structures, e.g. applied for catalytic reactions, new surface coatings, advanced drug design, smart materials, and so on.

5. Results and discussions

5.1. Experimental details

SnO_2 was selected as basic materials for showing SILD possibilities for gas sensor applications. SnO_2 has been one of the most widely studied metal oxides during the last decades due to its gas sensor and catalysis applications [1,2,6].

Single-crystalline Si and sintered quartz were used as substrates for deposition of SnO_2. Freshly prepared 0.01M solutions of SnF_2 were used as precursors during SnO_2 SILD. The samples were then washed with distilled water, to remove the excess of salt, and subsequently treated with 1.5M H_2O_2 solution. After this treatment, the excess H_2O_2 was removed by heating in air at T~80-100^oC. Each treatment step had a duration of 0.5 min.

For surface modification by SILD technology we used SnO_2 films with thickness ranging from 30-40 nm which were deposited by spray pyrolysis from $SnCl_4$-water solutions [6]. The reactants used in the synthesis of Ag^o were aqueous 0.01M solution of $AgNO_3$, as well as aqueous 0.1M solution of hydrogen peroxide with additions of KOH or ammonia (pH=9). Pd^o layers were made by repeated treatment of SnO_2 base by $PdCl_2$ (0.001M) solutions in ethyl. One Pd deposition cycle also included rinse in distilled water and treatment of SnO_2 samples with adsorbed Pd-ions in alcohol solutions heated at 50°C.

5.2. Structural properties of metal oxide films deposited by SILD

Typical SEM image of the surface morphology of undoped SnO_2 films deposited by the SILD method is shown in figure 1.

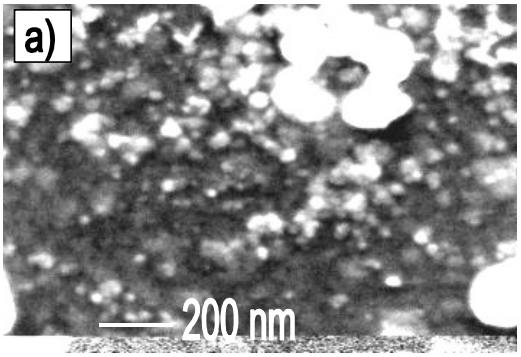

Figure 1. SEM images of SnO_2 films deposited on sintered quartz substrate after 20 cycles of deposition.

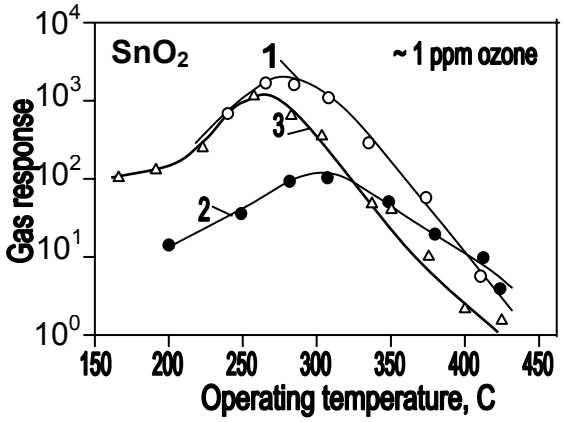

Figure 2. Temperature dependencies of SnO_2 gas response to ozone. Films deposited by SILD method using: 1- 20; 2-30; 3- 40 deposition cycles.

During study of the structure of metal oxides deposited by SILD method it was established that as-deposited films are amorphous or fine dispersed formation of hydrooxide or hydrated metal oxide-based compounds [7,8]. In the case of SnO_2 deposition such compounds are $Sn(OH)_4$ or $SnO_2 \cdot nH_2O$. The broad band on FTIR transmission spectra centered around 3250 cm^{-1} is a

confirmation of this conclusion. The main part of coordinated water, which can be responsible for the appearance of this band, is being removed from the film already after annealing at T_{an}=200 ^{o}C. FTIR study of deposited films have shown that after annealing hydroxides transform in oxide forms. However, traces of hydroxyl groups remain even after annealing at T_{an}=500 ^{o}C.

High degree of agglomeration is other peculiarity of metal oxides deposited from aqueous solutions. The undoped SnO_2 films deposited by the SILD method, as other metal oxides deposited from aqueous solutions, consist of spherical agglomerates and have very high roughness compared to the roughness of tin oxide films deposited by standard methods of film deposition. The SnO_2 films deposited by SILD showed a wide range of agglomerate sizes from 20 to 300 nm. The average agglomerate size increased with increasing number of deposition cycles, corresponding to increased overall film thickness. It indicates that the growth of the metal oxide films during deposition from aqueous solutions takes place through the growth of the agglomerates.

According to XRD measurements these agglomerates are fine-dispersed formations. On XRD patterns of as-deposited films, any diffraction peaks were not observed. Only after annealing at T_{an}>500^{o}C XRD diffraction peaks start to appear. These patterns were typical for polycrystalline material without preferred orientation. When T_{an} increases, these peaks become more narrow and intense. This observed evolution indicates on crystallite growth during heat treatment. However, this growth is not so strong in comparison with films deposited by sputtering or laser ablation.

5.3. Gas sensing properties of SnO_2 films deposited by SILD

Some results of gas response testing are presented in figure 2. It is seen that films have high gas response to ozone. The reaction of ozone detection is fast with response time at T_{oper}=275 ^{o}C of 2-3 sec. It is necessary to note that these films have better gas sensitivity to ozone than ceramics prepared by sol-gel method. Films deposited by SILD are sensitive to reducing gases, such as CO, H_2, CH_4, as well [7].

5.4. Surface modification of SnO_2 films by noble metals

The results of the influence of surface modifications of SnO_2 films by Pd and Ag on the gas sensing characteristics of SnO_2-based gas sensors are shown in figures 3 and 4.

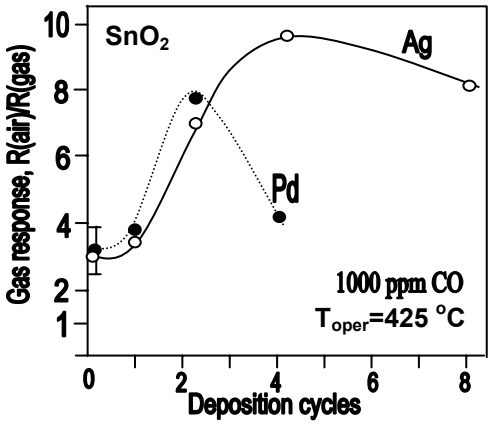

Figure 3. Influence of SnO_2 surface modification on gas response to CO.

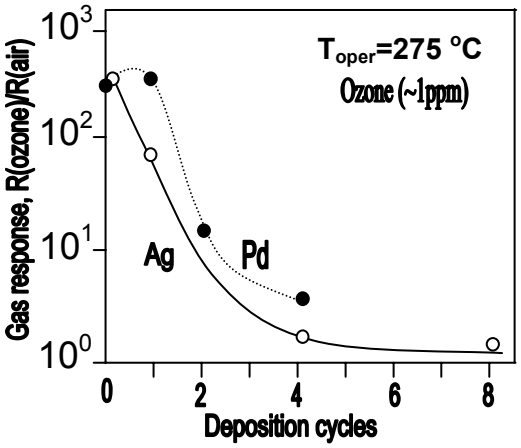

Figure 4. Influence of SnO_2 surface modification by Ag and Pd on gas response to ozone

These results have shown that Pd and Ag deposition on the SnO_2 surface promotes the increase of gas response to reducing gases by more than 5- 10 times. This demonstrates that this method of surface modification can indeed be used for improvement of SnO_2-based gas sensors. For both Pd and Ag, there exists some optimal surface coverage, which gives maximum increase of gas response. For Pd, maximum gas response to both H_2 and CO detection is obtained after two cycles of deposition. For Ag, the optimum is being observed at a greater extent of surface coverage, and this

optimum does not concur with H_2 and CO detection. For CO detection, the maximum gas response is obtained after four cycles of Ag^o deposition. Furthermore, the position of that optimum depends on operating temperature, shifting to the range with less Ag coverage while T_{oper} decreases. Another interesting effect, required understanding, is the influence of surface modification by Pd and Ag on sensor response to ozone. The presence of Pd, and especially Ag additives on the SnO_2 surface sharply suppresses the gas response to ozone. It was determined that already after two deposition cycles of Pd and Ag the gas response to ozone declines by more than 20 - 40 times for SnO_2:Pd samples, and by more than 100 times for SnO_2:Ag samples.

5.5. SnO_2 surface modification be metal oxides

First results of research in this direction were presented in [9]. Analyzing gas response of SnO_2 films with additional oxide layer of transition metals, such as Fe, Mn, Cu and Co, we established that such treatment really modifies characteristics of gas sensing matrix.

6. Conclusions

It was shown that SILD technology is effective method for preparing gas sensing films. SILD technology gives the possibility to deposit porous, rough metal oxide films with nano-scale crystallites having sizes smaller than 6-7 nm. As a results films deposited by SILD may have high gas response to both oxidizing and reducing gases. Films are agglomerated with average size of agglomerates equal to 20-80 nm.

SILD technology can be used for surface modification of metal oxide as well. This method permits to conduct a controlled deposition on the SnO_2 surface of clusters both noble metals, such as Pd and Ag, and metal oxides. Surface modification of SnO_2 films by Pd and Ag with using of SILD technology allows to improve gas response of SnO_2-based gas sensors to reducing gases, and to depress the sensitivity to oxidizing gases (ozone). This property of SnO_2 films modified by Pd and Ag can be used for improvement selectivity of SnO_2-based gas sensors. Metal oxide layers deposited on the surface of gas sensing matrix may be effective filters for improvement gas sensing characteristics as well.

7. Acknowledgements

This work was supported by the CRDF in the framework of CGP Program (Grant MO-E2-2588-CH-04)

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